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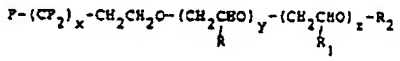
(54) Highly stable alcohol-containing foams and method for their production and use

Highly stable foams with high alcohol contents are obtained with surface-active foaming agents having the general formula



and methods are given for the production and use of the alcohol foams (33 06 593)

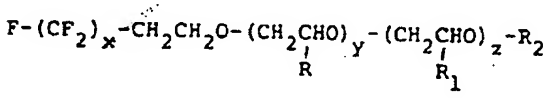
Handwritten:
Air under pressure is used here.
We have a pressureless system!

FCKW as propellant for aerosol foams!
M. Vys. 10/25/2005

BUNDESDRUCKEREI 08.83 308 038/706 13/80

Patent Claims

1. Stable foam with high alcohol content, consisting of a liquid phase of an alcohol or a mixture of alcohols and a surface-active foaming agent, which is nonionic and is selected from a compound or from a mixture of compounds having the general formula



in which

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x	is an integer or a mean value represented by an integer or a fractional number in the range of 2 – 12,
y and/or z	is an integer or a mean value represented by an integer or a fractional number in the range of 0 – 20,
R and/or R_1	stand for hydrogen or an aliphatic hydrocarbon group with 1 – 4 carbon atoms,
R_2	stands for hydrogen or an acyl group –CO-R_3, in which R_3 is an aliphatic hydrocarbon group with 1 – 4 carbon atoms,

and of a gas phase.

2. Foam according to Claim 1, characterized by the fact that the alcohol or the mixture of alcohols are lower alcohols and are chosen from the group of methanol, ethanol, n-propanol, i-propanol, and from mixtures of two or more alcohols of this group.

3. Foam according to Claim 1 or 2, characterized by the fact that the liquid phase contains the foaming agent in an amount of 0.1 to 2.0 weight %, based on the total weight of the liquid phase = 100.

4. Foam according to one of Claims 1 to 3, characterized by the fact that the liquid phase contains water.

5. Foam according to Claim 4, characterized by the fact that the liquid phase contains water in an amount of 1 to 50 weight %, based on the weight of the liquid phase = 100.

6. Foam according to one of Claims 1 to 5, characterized by the fact that the liquid phase contains a viscosity-increasing agent.

7. Foam according to Claim 6, characterized by the fact that the viscosity-increasing agent is selected from the group hydroxypropyl guar, hydroxyethylcellulose and polyvinylpyrrolidone.

8. Method for the production of a highly stable alcohol-containing foam, characterized by the fact that a surface-active foaming agent is added to a liquid consisting of one or several alcohols or their aqueous solution,
that the foaming agent is nonionic and is a compound or a mixture of compounds having the general formula

$$F-(CF_2)_x-CH_2CH_2O-(CH_2\underset{\underset{R}{|}}{C}HO)_y-(CH_2\underset{\underset{R_1}{|}}{C}HO)_z-R_2$$

in which

x	is an integer or a mean value represented by an integer or a fractional number in the range of 2 – 12,
y and/or z	is an integer or a mean value represented by an integer or a fractional number in the range of 0 – 20,
R and/or R_1	stand for hydrogen or an aliphatic hydrocarbon group with 1 – 4 carbon atoms,
R_2	stands for hydrogen or an acyl group –CO-R_3, in which R_3 is an aliphatic hydrocarbon group with 1 – 4 carbon atoms, and

that the liquid containing the foaming agent is treated with a gas or a gas mixture to form the foam. *Handwritten: Aerosol!*

9. Method according to Claim 8, characterized by the fact that the alcohols are low alcohols and are chosen from the group of methanol, ethanol, n-propanol, i-propanol, and mixtures of two or more of these alcohols.

10. Method according Claim 8 or 9, characterized by the fact that the foaming agent is added to the liquid in an amount of 0.1 to 2.0 weight %, based on the total weight of the liquid = 100.

11. Method according to one of Claims 8 to 10, characterized by the fact that the aqueous solution contains one or several low alcohols in an amount of 50 to 99 weight %, based on the weight of aqueous solution = 100.

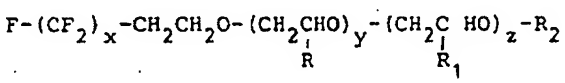
12. Method according to one of Claims 8 to 11, characterized by the fact that a viscosity-increasing agent is added to the liquid before the addition of the gas.

13. Method according to Claim 12, characterized by the fact that the viscosity-increasing agent is selected from the group of hydroxypropyl guar, hydroxyethylcellulose and polyvinylpyrrolidone.

14. Method according to one of Claims 8 to 13, characterized by the fact that the gas is chosen from the group of air, carbon dioxide and nitrogen.
Handwritten: "air" is circled, and highlighted with a question mark and exclamation point.

15. Method according to one of Claims 8 to 14, characterized by the fact that in the general formula of the selected surface-active foaming agent
x has a mean value of 8,
y = 2,
z = 0 and
R and/or R_2 stand for hydrogen.

16. Method for the treatment of a subterranean formation with a treatment liquid which is external to the formation, characterized by the fact that a foamed treatment liquid consisting of a foam phase and a liquid phase is used, and that the liquid phase consists of one or more alcohols or of their aqueous solution and a nonionic, surface-active foaming agent having the following general formula



in which

x	is an integer or a mean value represented by an integer or a fractional number in the range of 2 – 12,
y and/or z	is an integer or a mean value represented by an integer or a fractional number in the range of 0 – 20,
R and/or R_1	stand for hydrogen or an aliphatic hydrocarbon group with 1 – 4 carbon atoms,
R_2	stands for hydrogen or an acyl group $-CO-R_3$, in which R_3 is an aliphatic hydrocarbon group with 1 – 4 carbon atoms, and

that the foamed treatment liquid is introduced into the subterranean formation.

17. Method according to Claim 16, characterized by the fact that the alcohols are low alcohols, and are chosen from the group of methanol, ethanol, n-propanol, i-propanol, and mixtures of two or more of these alcohols.

18. Method according to Claim 17 or 18 [sic!], characterized by the fact that the foaming agent is added to the liquid phase in an amount of 0.1 to 2.0 weight %, based on the total weight of the liquid phase = 100.

19. Method according to one of Claims 16 to 18, characterized by the fact that the liquid phase is an aqueous solution of one or several alcohols and of the surface-active foaming agent, and that the alcohol or the alcohols are contained in the solution in an amount of 80 – 99 weight %, based on the total weight of the liquid phase = 100. *Handwritten: Plan B 50 – 79% alcohol.*

20. Method according to one of Claims 16 to 19, characterized by the fact that a viscosity-increasing agent is added to the liquid phase.

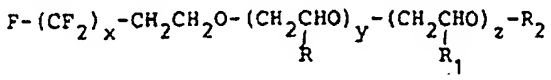
21. Method according to Claim 20, characterized by the fact that the viscosity-increasing agent is selected from the group of hydroxypropyl guar, hydroxyethylcellulose and polyvinylpyrrolidone and that an amount of 0.05 to 0.5 weight % of the viscosity-increasing agent is added to the liquid phase based on the total weight of the liquid phase = 100.

22. Method according to one of Claims 16 to 21, characterized by the fact that the gas of the foam phase is selected from the group of air, carbon dioxide and nitrogen.

23. Method according to one of Claims 16 to 22, characterized by the fact that in the general formula of the surface-active agent
x has a mean value of 8,
y = 2,
z = 0 and
R and/or R_2 stand for hydrogen.

24. Method according to one of Claims 16 to 23, characterized by the fact that a protective material is suspended in the foamed treatment fluid and when the support material containing treatment fluid is introduced into the subterranean formation, gaps are formed.

25. Method for the cleaning of surfaces, characterized by the fact that a foamed carrier liquid consisting of a foam phase and a liquid phase is used and that the liquid phase consists of one or several alcohols or of their aqueous solution and a nonionic surface-active foaming agent having the following general formula



in which

x	is an integer or a mean value represented by an integer or a fractional number in the range of 2 – 12,
y and/or z	is an integer or a mean value represented by an integer or a fractional number in the range of 0 – 20,
R and/or R_1	stand for hydrogen or an aliphatic hydrocarbon group with 1 – 4 carbon atoms,
R_2	stands for hydrogen or an acyl group –CO-R_3, in which R_3 is an aliphatic hydrocarbon group with 1 – 4 carbon atoms,

that at least one surface-cleaning agent is added to the foamed carrier liquid and that the surface is treated with the cleaning-agent-containing foamed carrier liquid.

26. Method according to Claim 25, characterized by the fact that the alcohols are low alcohols and are chosen from the group of methanol, ethanol, n-propanol, i-propanol and mixtures of two or more of these alcohols.

27. Method according to Claim 25 or 26, characterized by the fact that the foaming agent is added to the liquid phase in an amount of 0.1 to 2.0 weight %, based on the total weight of the carrier liquid = 100.

28. Method according to one of Claims 25 to 27, characterized by the fact that the liquid phase is an aqueous solution of one or several alcohols and of the surface-active foaming agent, and that the alcohol or alcohols are contained in the solution in an amount from 50 to 99 weight % based on the total weight of the carrier liquid = 100.

29. Method according to one of Claims 25 to 28, characterized by the fact that a viscosity-increasing agent is added to the carrier liquid.

30. Method according to Claim 29, characterized by the fact that the viscosity-increasing agent is selected from the group of hydroxypropyl guar, hydroxyethylcellulose and polyvinylpyrrolidone and that the liquid phase contains an amount from 0.05 to 0.5 weight % of the viscosity-increasing agent, based on the total weight of the liquid phase = 100.

31. Method according to one of Claims 25 to 30, characterized by the fact that the foam-forming gas is selected from the group of air, carbon dioxide or nitrogen.

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Patent Application

Halliburton Company, Duncan, Oklahoma, USA

Highly stable alcohol-containing foams and method for their production and use

The present invention concerns a highly stable foam with high alcohol content and a method for the formation and use of such foams. Foams of this type are especially suitable as carrier liquids for a wide variety of methods, including a method for the treatment of subterranean formations.

Foamed carrier and treatment fluids have been used so far in methods for the stimulation of subterranean formations and in industrial cleaning processes. The use of a foamed liquid for performing a stimulation process in a bore is especially advantageous, since the liquid phase in the foam takes up a smaller volume than with the usual liquids and consequently the liquid losses of the foam occurring in porous subterranean formations are lower. Furthermore the treatment liquid is removed rapidly from a treated formation because of the expandability of the gas phase in the foam. Foamed liquids are especially suitable for use as cleaving liquids for producing gaps in subterranean formations, by means of which the recovery of hydrocarbons from these formations is increased, because the foamed liquids have ideal properties for the suspension and transport of supporting material for the gap. For the cleaning of bores and in industrial cleaning processes, fine materials that were loosened are readily suspended in the foams and carried away by it. *Handwritten in margins: Air only under pressure expansion capability. In our case, pressureless!!*

Comment: Underlined in handwriting

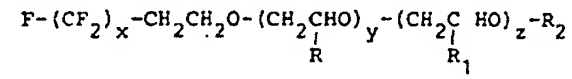
The liquids that have been used so far in the foams as a liquid phase were water, hydrocarbons or aqueous alcohol solutions. The use of one or more alcohols in the liquid phase of foamed liquids is especially advantageous in the treatment of subterranean formations that are sensitive to the penetration of water that is external to the formation.

In general, such water-sensitive formations contain clays that are damaged irreversibly through swelling and/or migration of fine materials upon contact with external water. The swelling of clays and/or migration of fine materials is less probable upon contact with alcohols or with an aqueous alcohol solution with a high alcohol content. Additionally, there are lower capillary pressures in the formation when alcohol-containing liquids are used, because a viscous structure of the water (on silicate surfaces) becomes less probable thereby, and the surface tension is reduced. This results in a more rapid and complete cleaning of the formation after treatment. Other factors that lead rapidly to production capability in a subterranean formation that was treated with a high alcohol content, are the higher vapor pressure of alcoholic liquids and the partial miscibility of oil and alcohol.

While, as was indicated above, foams of water-alcohol mixtures have already been used so far, such foams did not contain large amounts of alcohol in the liquid phase. This means that the foaming agents used so far could not form stable foams when the liquid phase had a high alcohol content.

The task of the present invention consists in producing a highly stable foam using an alcohol-rich liquid phase.

According to the invention this task is solved by selecting a stable foam with high alcohol content consisting of a liquid phase of an alcohol or a mixture of alcohols and a surface-active foaming agent that is nonionic and is selected from a compound or a mixture of compounds having the general formula



in which

x	is an integer or a mean value represented by an integer or a fractional number in the range of 2 – 12,
y and/or z	is an integer or a mean value represented by an integer or a fractional number in the range of 0 – 20,
R and/or R_1	stand for hydrogen or an aliphatic hydrocarbon group with 1 – 4 carbon atoms,
R_2	stands for hydrogen or an acyl group –CO-R_3, in which R_3 is an aliphatic hydrocarbon group with 1 – 4 carbon atoms,

and of a gas phase.

The highly stable foam according to the invention can be produced especially with low alcohols which so far have rather been considered more as defoaming agents than foaming agents. Low alcohols here are understood to mean organic alcohols with relatively few carbon atoms, that is, 1 – 3 carbon atoms.

A number of alkyl alcohols can be used for the liquid phase of the foams according to the invention. Among these, low alcohols or their mixtures are used preferably which are selected from the group of methanol, ethanol, n-propanol and i-propanol. As already mentioned, the liquid phase may consist of a pure alcohol or may contain water, that is, an aqueous alcohol solution can also be used. When using the alcohol-containing foams according to the invention as treatment liquids for the stimulation of subterranean formations, such as for the creation of gaps in the formation, the liquid phase preferably consists of 100% of alcohol or of an aqueous alcohol solution in which one or several alcohols are contained in an amount of 50 – 99 weight % based on the total weight of the liquid phase = 100.

In the formula of the foaming agent, the expression "a mean value represented by an integer or a fractional number" is to be understood to mean that the formula represents a mixture of compounds, in which the average values of x, y and z are integers, such as 8 or a fractional numbers such as 7.5, 7.8 or similar, in the given range.

In a further development of the invention, preferably the following nonionic surface-active substances are used:

(1) a nonionic, surface-active foaming agent corresponding to the formula given above with a mean value of 8 for x, y = 2, z = 0 and R and R_2 = hydrogen;

(2) a nonionic, surface-active foaming agent corresponding to the general formula given above with a mean value of 8 for x, y = 5, z = 0, R = methyl and R_2 = hydrogen.

(3) a nonionic, surface-active foaming agent corresponding to the general formula given above with a mean value of 8 for x, y = 2, z = 0, R and R_2 = hydrogen.

(4) a nonionic, surface-active foaming agent with the general formula given above with a mean value of 8 for x, y = 2, z = 2, R = methyl, R_1 and R_2 = hydrogen.

(5) a nonionic, surface-active foaming agent of the general formula given above with a mean value of 8 for x, y = 5, z = 0, R = methyl and R_2 = acetyl (R_3 = methyl).

Among the various nonionic surface-active foaming agents with the general formula given above, those are preferred most in which, in the formula, x has a mean value of 8, y = 2, z = 0 and R and R_2 are hydrogen.

The surface-active foaming agents described above form and stabilize foams made of alcohols or their aqueous solutions, that is, in the presence of one or more of the foaming agents in pure alcohol or in aqueous solutions with a high alcohol content, an addition of a gas or a mixture of gases such as nitrogen, air or carbon dioxide results in the formation of a highly stable foam.

As stated above, the nonionic, surface-active foaming agent is first combined with the base liquid, which can be an alcohol, a mixture of alcohols or an aqueous alcohol solution. In general, the foaming agent is combined with the alcohol-containing liquid in an amount of 0.1 to 2.0 weight %, based on the total weight of liquid = 100. During foaming of the mixture thus obtained, with nitrogen or another gas, a stable foam is formed. In order to increase foam stability, optionally a small amount of a viscosity-increasing agent can be added to the liquid before foaming. Such viscosity-increasing agents are, for example, hydroxypropyl guar, hydroxyethylcellulose or polyvinylpyrrolidone. In general, the viscosity-increasing agent is added to the basic liquid in an amount of 0.05 to 0.5 weight % based on the total weight of the basic liquid = 100.

When the alcohol-containing foams are used as carrier liquids to perform the treatment of subterranean formations, the foam is formed as described above from the surface-active foaming agent with one or several alcohols or their aqueous solutions, the basic liquid and other components contained in it are treated with a viscosity-increasing agent and then the liquid is foamed with a gas or a mixture of gases, such as air, carbon dioxide or nitrogen, preferably nitrogen. The foamed carrier liquid and the components contained therein are then introduced into the subterranean formation.

When using the foams according to the invention as carrier liquids or treating liquids for the treatment of water-sensitive, clay-containing subterranean formations, the liquid phase preferably consists of a pure alcohol, a mixture of alcohols or an aqueous

alcohol solution with a high alcohol concentration, that is, a concentration of 80 to 99 weight % of alcohol, based on the total weight of the liquid = 100.

In order to perform the creation of gaps in the subterranean formations to stimulate the recovery of hydrocarbons from these formations, the foams according to the inventions are used as cleaving liquids, whereby first the foam is formed in the manner described above. When a supporting material for the gap is to be suspended in the cleaving liquid, that is, introduced by the cleaving liquid into the gap formed and is deposited in there, the supporting material is first combined with the basic liquid and then the liquid is foamed as given above. Then the liquid is introduced into the formation.

When the foams according to the invention are used as carrier liquids in industrial cleaning processes, the foams are formed as indicated above with or without any added cleaning agent, and then is brought into contact with the surfaces to be cleaned, either by having the foam flow down over the surfaces or by having it remain in static contact with it.

As indicated above, the highly stable alcohol-rich foams according to the invention are especially suitable as carrier liquids or treatment liquids in methods for the treatment of subterranean formations, because the foams exhibit low liquid loss on porous formations, and when they come into contact with water-sensitive materials in the formations, they damage these less.

The preparation of the foaming agent for the foam according to the invention and the treatment method according to the invention are performed as described below:

Alcohols with perfluorinated groups are reacted with oxiran or substituted oxirans. This reaction is carried out under anhydrous conditions and is catalyzed by a Lewis acid. This reaction is carried out according to one of the following methods or their variations.

First, the alcohol with the perfluorinated...[Line 30 on page 17 is illegible – Translator]...into the autoclave and then an amount of the oxiran or of the substituted oxiran or a mixture of these is introduced at such a rate that the reaction temperature is held at a value between 60 and 140°C. The reaction is catalyzed by a Lewis acid, preferably antimony pentachloride and at the same time other catalysts can be introduced with the addition of the oxiran compounds. The oxiran compounds are added in such

amounts that the molar ratio of alcohol with the perfluorinated group to the oxiran compound lies between 1:4 and 1:10, whereby values between 1:6 and 1:8 are most preferred. The reaction rate can be controlled by the combination of temperature and catalyst concentration.

After the oxiran compound has been completely added, the autoclave is kept at a temperature of at least 80°C until the reaction is completed. Preferably, the autoclave is held at a temperature of at least 100°C for at least 30 minutes after the complete addition of the oxiran compound. Then the autoclave is cooled and a sample of the reaction product can be taken for analysis or for performing other chemical reactions. More oxiran compound can also be added in order to obtain higher molar ratios between the oxiran compound and the alcohol with the perfluorinated group or in order to vary the type of oxiran groups in the end product. The reaction can be monitored conveniently by gas chromatographic analysis of unreacted oxiran compounds. An adduct is most preferred, the residual oxiran content of which is 0.2 weight % or less.

All the above mentioned reactions, depending on their type, must proceed in the absence of water, and are carried out in an inert gas such as nitrogen. The foaming agent for the foam according to the invention in which in the general formula given R_2 = acetyl is prepared and the treatment method according to the invention is performed according to conventional methods by reaction of the products obtained as described above with acetic anhydride.

For better understanding of the highly stable alcohol-containing foams and the method according to the invention, some examples will be given below.

Example 1

Some of the above nonionic surface-active foaming agents are dissolved through stirring in pure methyl alcohol in a volume ratio of 10:1000. Aliquots of 500 mL of the solution thus obtained are introduced into a liquid container under nitrogen pressure. The liquid is pressed out from the container through a mixing nozzle. A separate stream of nitrogen under pressure is introduced in the liquid in the mixing nozzle, whereupon the liquid becomes foamed. The foam obtained is expelled from the mixer under atmospheric pressure and is collected in a measuring cylinder of 500 mL.

The time is measured within which half of the liquid settles from the foam that was formed as described above. The longer the half-settling time the greater the stability of the foam.

The quality of the foam, that is, the volume content of the gas in percent, is also determined. Higher foam qualities show good uptake of the gas in the liquid phase.

The results of the experiments are represented in Table I below.

Table I

Quality and half-settling time of the methyl alcohol foams

Foaming agent						Half-settling time	Quality
x	y	z	R	R_1	R_2	minutes	Volume%
8	8	0	H	-	H	0:25	56
8	6	0	H	-	H	0:46	59
8	4	0	H	-	H	2:20	70
8	2	0	H	-	H	4:30	70
8	0	0	-	-	H	4:00	73
8	12	0	CH_3	-	H	0:12	56
8	8	0	CH_3	-	H	0:18	65
8	6	0	CH_3	-	H	1:05	60
8	5	0	CH_3	-	H	1:50	60
8	4	0	CH_3	-	H	2:35	63
8	2	0	CH_3	-	H	0:36	76
8	2	1	CH_3	H	H	2:50	68
8	2	2	CH_3	H	H	0:43	66
8	5	1	CH_3	H	H	0:15	61
8	5	2	CH_3	H	H	0:11	57
8	5	0	CH_3	-	$COCH_3$	0:14	61
8	2	2	H	CH_3	H	1:55	64
FC-431						0:10	48

FC-431 is a commercially-available formulation with a perfluoro-substituted sulfonamide produced by the 3M Company, Saint Paul, Minnesota.